

Inorganometallic Catalyst Design Center (ICDC)

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Lead Institution: University of Minnesota

Start Date: August 2014

Mission Statement: *To guide the discovery of superior catalysts by integrating computational modeling with experiments in well-defined systems that are amenable to high-throughput search and discovery.*

The **vision** of the ICDC encompasses accelerating the development of supported cluster catalysts with the following characteristics:

- **Uniform mesoscale structures** that can be synthesized reproducibly, which are ideal for both full experimental structural characterization and computational modeling.
- **Clusters** that are well-defined and uniform in structure and composition, but isolated from each other on supports to minimize cluster-cluster interactions and agglomeration/sintering.
- **Catalyst structures** amenable to high-throughput experimental screening, very reliable quantum mechanical predictions on prototype exemplars, and computational high-throughput screening.

There are remarkably few experimental examples of well-defined supported subnanometer cluster catalysts due to the challenge of synthesis and limits of stability. The primary examples are supported metal clusters, for which a few highly selective and active catalysts have been described. Critical factors are cluster size, shape, composition, and positioning of atoms/ions of specific metals when the clusters comprise more than one type of metal atom/ion. ICDC studies how these various factors affect adsorption properties, stability, reaction rates and selectivity.

The potential number of candidate cluster catalysts is enormous, making it impractical to synthesize even a modest fraction of them, much less to characterize their structures, physical properties, and catalytic efficacy. Therefore, ICDC guides the selection of synthesis targets computationally. Furthermore, we develop and demonstrate synthesis strategies that are very broadly applicable.

An ultimate goal of the computations is high-speed (high-throughput) predictive characterization of putative cluster structures, stabilities, and catalytic competency to yield a database of potential catalysts that is unparalleled in size and chemical diversity. Powerful, newly developed quantum chemical methods have predictive accuracy for complex catalytic problems that were not amenable to reliable theoretical predictions as recently as ten years ago. Data mining for these hypothetical structures, together with strategic implementation of high-level theory for specific hypothetical and real examples and for novel synthetic strategies will accomplish the following **strategic objectives**:

- **Provide sufficient information** about how newly synthesized catalysts guide reactions through sequences of elementary steps, some of which pertain to more than one process.
- **Develop** new strategies and methods for computationally-guided discovery of useful catalysts.
- **Design** new methods for rapid synthesis of previously unexplored well-defined catalytic clusters, including those with compositions unattainable on the macroscopic scale, on supports that both isolate the clusters and offer easy access to reactants.
- **Develop** new approaches for the discovery and theoretical explanation of structure/function relationships in catalysts in the largely unexplored cluster size range < 200 atoms.

The specific scientific focus and challenge is the energy-efficient liquefaction of natural gas, either by catalytic conversion to alcohols or by catalytic conversion of C1, C2, and C3 species to C6 to C10 hydrocarbons. It requires the mastery of a set of generic reactions - the key being catalysis. Despite the very specific technical focus, we anticipate that much of what is learned about catalyst design and discovery will prove transferrable to other important problems in chemical catalysis. The ability to test

hypotheses *in silico*, followed by experimental validation, over an enormous and arbitrarily modifiable database of hypothetical catalysts is expected to lead to compelling, transferrable catalyst design rules and potentially lead to the discovery or design of new mechanisms and desirable new catalytic chemistry. Computational design, screening, and synthesis is complemented by high-throughput experimental screening enabled by the expertise and instrumentation developed by Center members at The Dow Chemical Company.

One key to achieving experimentally uniform clusters in this critical mesoscale size range is the use of highly uniform mesoporous metal-organic frameworks (MOFs) and surface-supported porphyrins as

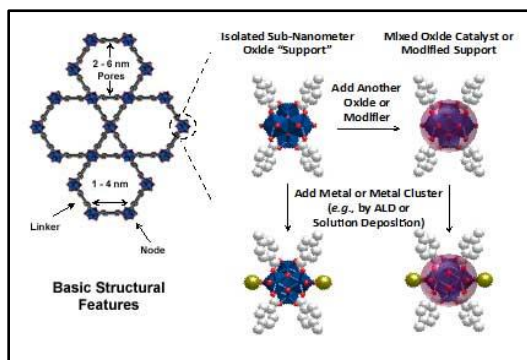


Figure 1. Schematic of the new class of materials

scaffolds and supports, or for cluster buildup activity, selectivity and lifetime. The key feature of the new materials is an array of "nodes" that have large and controllable separations, with only organic linkers between them (see Fig. 1.).

Research Strategies. ICDC is organized by **research themes:** a) Quantum Simulations and Computational Screening, b) Novel Material Synthesis, c) Material Characterization, and d) Catalysis. The early experimental work was driven by experience-based hypotheses, with the goal of moving toward computationally-driven design as the Center matures, always directed toward specific

reactions of high interest to DOE. The research, therefore, has two sides that map to the four research themes:

1. Hypothesis-driven work to develop catalytic material structure/function relationships for target reactions, using synthesis, characterization, catalytic assessment, and modeling/computations to explain observations and suggest new materials.
2. Work to develop new experimental and theoretical methods and tools to explain observations and suggest new materials. Progress is achieved by investigating target reactions with available computational and experimental techniques. The results of the simulations help to achieve a fundamental understanding of the materials and their catalytic activities, inspire new experiments, and reveal more clearly where computational tools need improvement.

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